11 SULFUR

Sulfur along with calcium and magnesium is listed as a secondary plant nutrient. Because the criterion for grouping plant nutrients as primary, secondary, or micro is based on their amounts removed by the crop plant, it may not be long before this classification of plant nutrients has to be reexamined because sulfur and magnesium are taken up by the crop plants in about the same amounts as phosphorus. In some instances calcium may be taken up in even larger amounts than phosphorus by some species. Crop uptake of S in relation to P, as well as in relation to N, is shown in Figure 11.1. Sulfur uptake by most crops is 10 to 15% of N uptake. S uptake by crops in relation to P varies considerably. While in rapeseed-mustard S uptake is about 175% of P uptake, in most other oilseed crops in general uptake is about the same for S and P. In cereals S uptake is about 60 to 75% that of P.

Over the years there have been increasing reports from all parts of the world, especially the tropics and subtropics (Pasricha and Fox, 1993), of sulfur deficiency in crop plants and responses of crops to sulfur. Australia (Anderson, 1952), the United States (Mitchell and Mullins, 1990; Rechcigl, 1992), Central America (Raun and Barreto, 1992), India (Tandon, 1992, Kumar et al., 1992), and Pakistan (Rashid et al., 1992) are some of these countries. This is primarily due to the following reasons:

- 1. Increased use of high-analysis fertilizers, which contain no or only traces of sulfur; for example, the use of diammonium phosphate (DAP), urea ammonium phosphate (UAP), and ammonium polyphosphates (APP) in place of ordinary superphosphate and the use of urea or ammonium nitrate in place of ammonium sulfate.
- 2. Increased crop yields due to the introduction and cultivation of nitrogen-responsive, high-yielding hybrids, composites, and varieties of cereals, resulting in rapid depletion of soil sulfur.
- 3. Reduction in the emission of sulfur dioxide (SO₂) due to environmental pollution control regulations. In the United States SO₂ emission from the combustion of fossil fuels, petroleum refining, and other industries declined from 32 million Mg (18 million Mg sulfur)

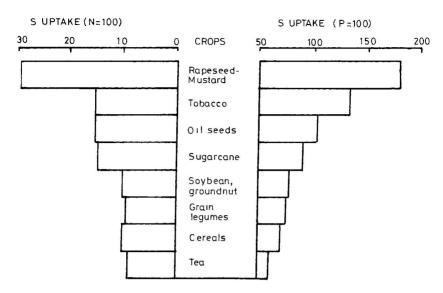


Figure 11.1. Crop uptake of S in relation to N and P uptake. (Adapted from Tandon, 1991.)

in 1972 to 26 million Mg (13 million Mg sulfur) in 1980 (Tisdale et al., 1985). A contour map of sulfate concentration in rain in different parts of the United States for the period 1979 to 1982 is shown in Figure 11.2. Sulfate concentration in rain was highest in the Michigan and southern Ontario region of the United States and Canada followed by that in the upper Chesapeake Bay region of the East Coast. It was much less in the northwest, central, and southern United States. Since most of the emitted SO₂ returns to the soil in rainfall (acid rain), this source of replenishment of soil sulfur is declining. Estimates range from 1 kg S ha⁻¹ yr⁻¹ in rural areas to about 100 kg S ha⁻¹ yr⁻¹ near industrial townships. This is just a small component of the entire S cycle (Figure 11.3).

4. Decreased use of farm manure even in developing countries.

11.1. SULFUR IN SOILS

Total S in soils may vary from a few to 1000 mg S kg $^{-1}$ soil (0.1%); higher values can be encountered in problem soils such as saline and acid-sulfate soils (Takkar, 1988; Ganeshmurthy et al., 1989). Sulfur in soils is present both in organic and inorganic forms. While inorganic forms are important because most of the S is taken up by plants as SO_4^{2-} (sulfate), organic forms are important because they often make up the bulk of soil S. Because S is an integral part of soil organic matter, total S is generally greater in fine-textured than in coarse-textured soils. In general, soils containing greater amounts of organic matter contain a larger fraction of their S in organic form.

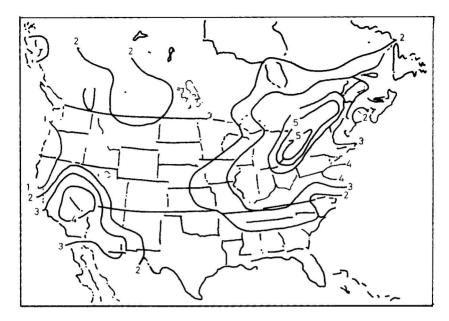


Figure 11.2. Precipitation weighted sulfate concentration contour map of North America for the period 1979–1982. (From Mohnen and Wilson, 1985. *Acid Rain in North America: Concepts and Strategies*, p. 441. With permission of Plenum Press).

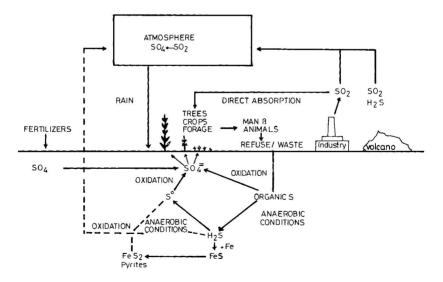


Figure 11.3. Sulfur cycle.

11.1.1. Organic S

Since the bulk of S in plant tissue is present as the S-containing amino acids cystine, cystein, and methionine, organic S is generally associated with proteins in plants and in their residue when added to the soil. S is therefore as much an integral part of soil organic matter as N, and the N:S ratio in most non-saline soils falls within the narrow range 6 to 8:1 (Tisdale et al., 1985). Most of the biological processes involved in mineralization of organic N in soils therefore are also important in organic S mineralization.

Well over 90% of the S in surface layers of well-drained, nonsaline soils is present in organic form. Organic S is divided into two major groups, namely, C-bonded S (amino acids) and non-C-bonded S (ester sulfates such as phenolic sulfates and sulfated polysaccharides). Non-C-bonded S is reduced to $\rm H_2S$ by hydriodic acid (HI) and is estimated this way. Carbon-bonded S can be estimated by subtracting non-C-bonded S from total organic S (Stevenson, 1987). In a study involving 24 Australian soils, organic S was 93% of total S; of this, 52% was non-C-bonded and 41% was C-bonded (Freney, 1967).

11.1.2. Inorganic S

Inorganic S in most soils is present as SO_4^{2-} ions associated with monovalent (Na, K) and divalent cations (mostly with Ca and Mg; traces with Cu, Mn, Zn, and Fe). Sulfate salts present in the soil solution (soluble S) may be adsorbed onto soil colloids, or the salts may be present as insoluble compounds.

Soluble S. The sulfate content of the soil solution (soluble S) is variable and depends upon a number of factors.

- 1. Weather conditions, particularly temperature that determines the rate of mineralization of soil organic matter.
- 2. Precipitation heavy rains can lead to excessive leaching.
- 3. Associated cations leaching losses are greatest when monovalent cations such as Na and K are mostly associated with sulfate.
- 4. Soil water content soil water affects sulfate content in soil solution in two ways. First of all, the sulfate concentration in soil solution generally decreases as the water content increases (dilution effect). Secondly, as a soil dries out due to high evapotranspiration rates, sulfate from lower soil layers moves upward by capillary action with water and increases the concentration of sulfate in the surface-layer soil solution. With sufficient drying, sulfates may then precipitate on the soil surface, particularly calcium sulfate.
- 5. Application of sulfur containing fertilizers as expected, this will increase soil solution sulfur content.

A soluble-S content of 5 mg kg $^{-1}$ soil is generally adequate for the growth of most crops; Brassicas require somewhat more S.

Adsorbed S. Sulfur as SO₄²⁻ can be adsorbed on clay minerals by salt adsorption; on hydroxides and oxyhydroxides of iron and aluminum, which acquire a positive charge under low-pH conditions; and on soil organic matter, which develops positive charges under certain conditions.

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Among the clay minerals 1:1 layer silicates such as kaolinite adsorb more sulfate than 2:1 layer silicates. Due to sulfate retention tendencies of hydroxides and oxyhydroxides of aluminum and iron (more in aluminum), adsorbed sulfate is an important fraction of the total S contributing to crop plants on oxisols and many ultisols. Such soils are generally low in soil organic matter and also release of organic S is likely to be slow. Adsorbed S is also an important component in the subsoils of these soils, which are generally very low in organic matter content. Also sulfate leached from surface soils tends to accumulate in subsoil, either by precipitation or adsorption.

Insoluble S. Calcium sulfate can coprecipitate with calcium carbonate and this coprecipitated sulfate forms an important fraction of total S in calcareous soils. Unless brought into solution, which is difficult and very slow, this form of S is relatively unavailable to plants. A number of factors, particularly the size of the calcium carbonate particles, common ion effects, and soil water content determine the rate of dissolution of insoluble S. Grinding of soil samples while preparing it for analysis may reduce the particle size of calcium carbonate and may lead to increased dissolution of insoluble S. This results in higher available S values as determined in a soil test.

Soils in arid and semiarid regions have large deposits of gypsum (CaSO₄ 2H₂O). When mined and used for reclaiming sodic soils, gypsum also adds large amounts of S to soils. As a matter of fact gypsum is a an extremely cheap source of S and is being used in India for this purpose. Often sodic soils may have a layer of gypsum deposited in the subsoil which, if mixed with the surface (deep plowing) can solubilize the exchangeable Na⁺ and help reclaim the sodic soil.

Under submerged soil conditions SO_4^{2-} present in soil is reduced to H_2S (sulfide). Also, the anaerobic decomposition of soil organic matter leads to the production of H_2S (this is the reason for the foul smell coming from swamps). Because reduced soil conditions also lead to the transformation of Fe^{3+} to Fe^{2+} , the presence of H_2S leads to the precipitation of S as iron sulfide, which later undergoes conversion to pyrite (FeS_2). Pyrite is the principal insoluble-S form in flooded rice paddies. Availability of this form of S requires the oxidation of pyrites.

11.2. ELEMENTAL SULFUR AND ITS OXIDATION

As discussed earlier, H_2S and FeS_2 are produced under anaerobic conditions. Under the same reduced conditions in some instances elemental S° may also be deposited. In well-drained soils elemental S or H_2S is oxidized to SO_4^{2-} .

This oxidation is brought about by *Thiobacilli* (*T. thioxidans*, *T. thioparus*, *T. ferrooxidans*, etc.) (Kuenen, 1975; Starkey, 1966), which are a group of autotrophic bacteria that derive their energy from the oxidation of S to SO_4^{2-} for the fixation of CO_2 into organic matter. The general equation, as given by Tisdale et al., (1985), is as follows:

$$CO_2 + S + 1/2 O_2 + 2 H_2O \rightarrow [CH_2O] + SO_4^{2\pm} + 2 H^+$$

Oxidation of elemental S to SO₄²⁻ by *Thiobacilli* is controlled by a number of factors, including soil pH, temperature, and aeration. *Thiobacillus thiooxidans* grows best in the pH range 1.0 to 4.0, while *T. thioparus* has an optimum pH range of 4.5 to 7.5 (Tisdale et al., 1985). Thus S oxidation is most rapid under low soil pH conditions (this is in contrast to nitrifying bacteria, which perform best in neutral or somewhat higher soil pH). Regarding temperature, the oxidation of S proceeds most rapidly between 20 and 40°C. S-oxidizing bacteria need oxygen, and their activity is reduced when anaerobic conditions prevail. Normally, well-drained soils suitable for most crops are also suitable for S-oxidizing bacteria.

Under anaerobic conditions the oxidation of S may be carried out by photosynthetic bacteria *Chlorobium*, the green S bacteria, and *Chromatium*, *Thiocystis*, and *Thiocapsa*, the purple S bacteria (Fenchel and Blackburn, 1979). These bacteria can also oxidize H_2S with the intermediate production of S° , but are inhibited by high concentrations of H_2S ; the tolerance limits are 4 to 8 mM L⁻¹ for green bacteria and 0.4-2 mM L⁻¹ for the purple bacteria (Pfening, 1967). Photosynthetic S° oxidation is dependent on light and a source of reduced S compounds; such a situation is present on marine muds and sands, where sulfide diffuses from below and oxygen penetration is low. Such a habitat is known as "sulfuretum" (Fenchel and Blackburn, 1979). The general equation as given by Tisdale et al. (1985) is as follows:

$$CO_2 + 2 H_2S \rightarrow [CH_2O] + H_2O + S^\circ$$

11.3. OXIDATION OF PYRITES

The pyrite oxidation cycle as given by Fenchel and Blackburn (1979) is shown in Figure 11. 4, The organism responsible is *Thiobacillus ferroxidans*, which can also oxidize elemental S and reduce S compounds such as H₂S. *T. ferroxdians* is found where pyrite is exposed to atmospheric O. The initial process of pyrite oxidation as given by Fenchel and Blackburn (1979) is as follows:

$$2 \text{ FeS}_2 + 2 \text{ H}_2\text{O} + 7 \text{ O}_2 \rightarrow 2 \text{ Fe}^{2+} + 4 \text{ SO}_4^{2\pm} + 4 \text{ H}^+$$
 (1)

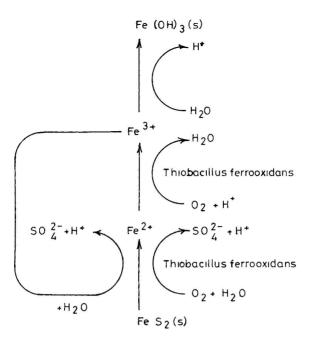


Figure 11.4. The pyrite oxidation cycle. (From Fenchel and Blackburn, 1979. *Bacteria and Mineral Cycling*, p. 225. With permission of Academic Press.)

Ferrous is further oxidized to Fe³⁺

$$4 \text{ Fe}^{2+} + \text{O}_2 + 4 \text{ H}^+ \rightarrow 4 \text{ Fe}^{3+} + \text{H}_2\text{O}$$
 (2)

The Fe³⁺ formed is itself an oxidant and oxidizes pyrite abiologically as below (at low pH values):

$$FeS_2 + 14 Fe^{3+} + 8 H_2O \rightarrow 15 Fe^{2+} + 2 SO_4^{2\pm} + 16 H^+$$
 (3)

Fe²⁺ produced works as a substrate for *T. ferrooxidans*. As the pH of the effluent water increases, the Fe³⁺ is hydrated to Fe(OH)₃, which precipitates.

$$Fe^{3+} + 3 H_2O \rightarrow Fe(OH)_3 + 3 H^+$$

Pyrite oxidation can also take place abiologically, but the rate is greatly increased (by a factor of 10⁶) when *Thiobacilli* are involved. Oxidation of pyrites is important when used as a soil amendment for reclaiming sodic soils.

11.4. ASSESSING S NEEDS OF SOILS

A number of methods for estimating available S in soils have been proposed by several workers; the most common among these are as follows:

- 1. Calcium chloride extractable
- 2. Heat-soluble S
- 3. Monopotassium or monocalcium phosphate (500 mg P L^{-1}) solution extractable
- 4. Morgan's extract (sodium acetate-acetic acid buffer of pH 4.0)
- 5. 0.5 N ammonium acetate + 0.25 N acetic acid extractable
- 6. Olsen's 0.5 M sodium bicarbonate extractable S

Critical levels for some crops in India for different extracting solutions are given in Table 11.1. The critical levels are usually in the range of 11 to 13 mg S kg^{-1} soil with calcium chloride, monopotassium phosphate, heat-soluble, and Morgan's extracting-solution methods.

One needs to remember that critical levels of S will vary with the method of analysis, soil type, and crop, and therefore critical levels need to be determined for different crops grown under different soil-climate conditions.

Sulfur recommendations in the United States vary from state to state, and within a state these differ for soils and crops. In Maryland the recommendation for sandy or sandy loam soils for corn, soybean, and small grains are 44 kg S ha⁻¹ when calcium phosphate extracted SO_4^{2-} -S is less than 6 mg kg⁻¹ soil; lesser amounts are recommended for soils testing higher. The recommendations in southern states (South Carolina, Alabama, Arkansas, Louisiana) in general are for lesser amounts (11 kg S ha⁻¹) for crops other than forages; for forages the recommendations in Louisiana and Arkansas are from 28 to 56 kg S ha⁻¹ (Messick, 1992).

A soil test for available S generally determines the inorganic SO_4^{2-} -S in soil at the time of sampling, but does not estimate the amount of S that may be available to a crop during its growth period from the oxidation of soil organic matter, from the subsoil reserves, and that which may be added by rain. Researchers in Oklahoma, South Dakota, and Wisconsin have therefore developed models to account for various aspects of the S cycle (Messick, 1992). However, a large database is necessary for making the models predictable and more useful than the routine soil testing.

11.5. SULFUR DEFICIENCY SYMPTOMS IN PLANTS

The behavior of S in plants is similar to N, a corollary to the similarity of S and N in regard to function in the plant and distribution in the soil. Sulfur deficiency in plants resembles N deficiency, and S deficient plants also turn pale yellow. However, S is less mobile than N in plants, and the younger leaves

Table 11.1 Critical Levels of Available Soil-S (ppm) for Different Crops According to Common Methods of Extraction

Crop	CaCl ₂	KH ₂ PO ₄	CaH ₂ PO ₄	Morgan	AmAc	Heat-S	Olsen	Mean
Rice	10	10	10	13	11	16	20	12.8
Wheat	13				25	13		17.0
Maize	13	10	14	25	30			15.5
Groundnut	10					11		10.5
Rapeseed-mustard	10	13	13	10	9			10.4
Sunflower	18	10			30			18.8
Soybean	14		14	8	8		18	12.4
Clusterbean				10		10		10.0
Alfalfa		9				20		14.5
Mean	12.6	10.4	12.7	13.2	18.8	14.0	19.0	

Adapted from Tandon 1992. Sulfur Agric. 16:20-23. With permission of The Sulfur Institute, Washington, D.C.

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Table 11.2 Denciency and Sufficiency Levels of 5 in Flants					
Crop	Part of plant sampled	Deficient Sufficient (g kg ⁻¹ dry matter)			
Alfalfa	Whole tops at bud stage (10% bloom)	1.5–2.3	2.3		
Barley	Boot-stage tissue	1.2	1.4		
Wheat	Boot-stage tissue	1.2	1.4		
Soybeans	Upper, fully developed, trifoliate leaves prior to pod set	1.4	2.2–2.8		
Tobacco	Leaves	1.1-1.8	1.5 - 2.6		
Red clover	Whole tops at bud stage (10% bloom)	2.0 (critical)			
Cauliflower	Whole tops at the curd stage	1.8	1.9		
Rapeseed-mustard		2.1 (critical) ^a			
Pigeon pea	Shoots before flowering	1.34 (critical) ^b			
Groundnut	Plant	2.0 (critical) ^c			

Table 11.2 Deficiency and Sufficiency Levels of S in Plants

Adapted from the Authority of the Atlantic Provinces Agricultural Services Coordinating Committee, Canada (1988).

may generally turn pale yellow, while the older leaves may remain green. Note that the reverse is the case in N deficiency. There are frequent exceptions to these symptoms, however. The general deficiency symptoms are pale yellow, stoopy plants with short and slender stalks; these symptoms will not disappear with N application. Plant species differ considerably in expressing S-deficiency symptoms. Deficiency and sufficiency levels of S in the different plant parts for some crops are given in Table 11.2.

11.6. SULFUR NEEDS OF CROPS

Crops and cultivars within crops vary considerably in their S requirements. Spencer (1975) has divided crops into three broad groups (Table 11.3). Group I includes Crucifers and *Brassicas* which have high S requirement (20 to 80 kg S ha⁻¹). Group II includes plantation crops, which have moderate S requirements (10 to 50 kg S ha⁻¹). Group III includes cereals, forages, and other field crops and has low S requirement (5 to 25 kg S ha⁻¹). As a rule of thumb, Tandon (1991) gives the following S requirements (kg S Mg⁻¹ grain): 3 to 4 kg for cereals, 8 kg for grain legumes (beans), and 12 kg for oilseeds (rapeseed mustard, sunflower, groundnut, soybeans, etc.).

^a Pasricha et al. (1988)

^b Singh (1991)

^c Cheema and Arora (1984)

Table 11.3 A Tentative Classification of Crops According to Their S Fertilizer Requirement

	- · · · · · · · · · · · · · · · · · · ·			
Crop	Fertilizer requirement in deficient areas ^a kg S/ha			
Group I (high)				
Cruciferous forages	40–80			
Alfalfa	30–70			
Rapeseed	20–60			
Group II (moderate)				
Coconuts	50			
Sugar cane	20–40			
Clovers and grasses	10–40			
Coffee	20–40			
Cotton	10–30			
Group III (low)				
Sugar beet	15–25			
Cereal forages	10–20			
Cereal grains	5–20			
Peanuts	5–10			

^a Figures cited for the high end of the range apply where the potential yield is high, accessions in rainfall are low, the soil is low in available S, and there is considerable loss in effectiveness of applied S. Figures cited for the low end refer to the opposite situation. For perennials, a further consideration is whether the requirement refers to a corrective fertilizer dressing or to an annual maintenance dressing. The amount for the former is typically about four times that of the latter.

From Spencer. 1975. Sulfur in Australian Agriculture, K.D. McLachlan, Ed., p. 103.

11.7. SULFUR FERTILIZATION

Sulfur has been applied in the past along with ammonium sulfate, ordinary superphosphate, and potassium sulfate. However, with the advent of high-analysis fertilizers such as anhydrous ammonia, urea, diammonium phosphate (DAP), and ammonium polyphosphate (APP), application of S has been gradually reduced. Thus, where necessary, additional S may be applied as elemental S, gypsum, or pyrite, depending upon the availability of the material and the needs of crops and soils. The most common S and S-containing fertilizer materials are listed in Table 11.4.

Table 11.4 Sulfur and Sulfur Containing Fertilizer Materials

Fertilizer	Chemical composition	S content (%a)
S Fertilizers		
Elemental S	S	99.6
Agric-S	S	90.0
Gypsum	$CaSO_4 \cdot 2H_2O$	18.6
Commercial gypsum	$CaSO_4 \cdot 2H_2O + impurities$	13–14
Pyrites	FeS_2	53.5
N Fertilizers		
Ammonium sulfate	$(NH_4)_2SO_4$	23.7
Urea sulfur	,	10
Ammonium phosphate sulfate	$(NH_4)_2SO_4 + NH_4H_2PO_4 + (NH_4)_2HPO_4$	15.5
P Fertilizers		
Ordinary superphosphate (OSP)	$Ca(H_2PO_4)_2 + CaSO_4 \cdot 2H_2O$	13.9
Concentrated superphosphate (CSP)	$Ca(H_2PO_4)_2$	1.5
Ammoniated OSP		12
Ammoniated CSP		1.4
K Fertilizers		
Potassium sulfate	K_2SO_4	17.6
Potassium magnesium sulfate	$K_2SO_4 \cdot 2 MgSO_4$	22.0
Others		
Copper sulfate	$CuSO_4 \cdot 5H_2O$	12.8
Zinc sulfate	$ZnSO_4 \cdot H_2O$	17.8
Manganese sulfate	$MnSO_4 \cdot 4H_2O$	14.5
Magnesium sulfate (Epsom salt)	$MgSO_4 \cdot 7H_2O$	13.0
Ammonium thiosulfate	$(NH_4)_2S_2O_3$	43.3

^a Commercial grades generally contain somewhat lesser values.

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